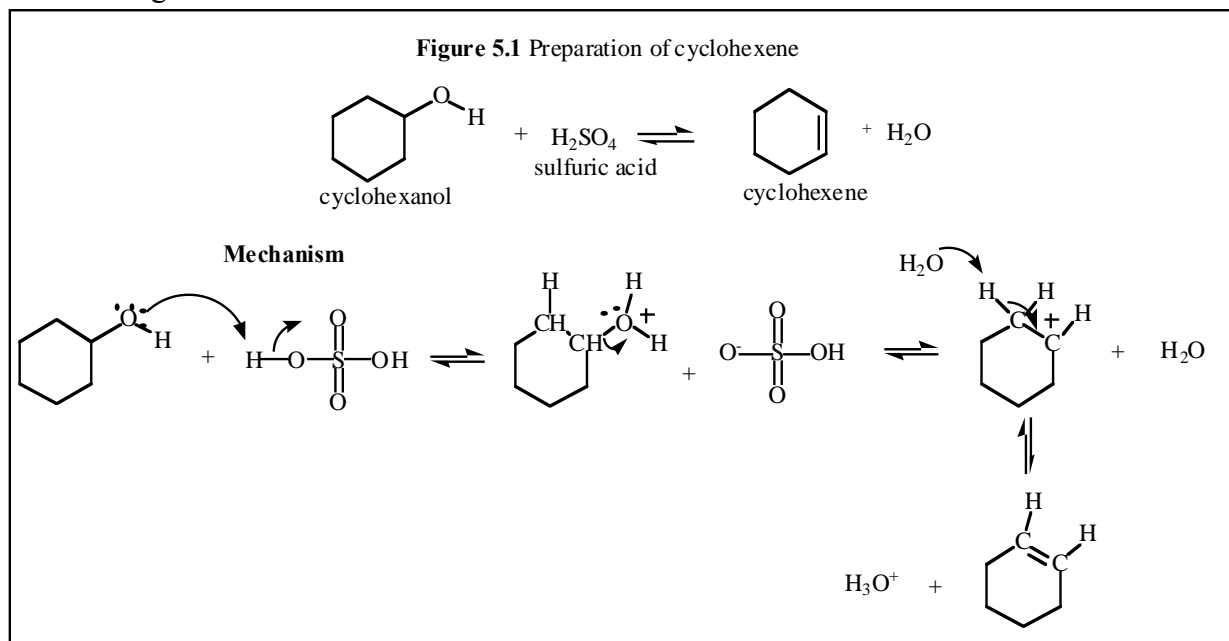


## Experiment 5 Preparation of Cyclohexene

In this experiment we will prepare cyclohexene from cyclohexanol using an acid catalyzed dehydration reaction. We will use the cyclohexanol that we purified in our previous experiment. The reaction involved is shown in Figure 5.1.



This is an acid-catalyzed dehydration reaction. The first step is the reversible protonation of the oxygen atom of the alcohol. The lone pair of the oxygen, acting as the base, attacks the proton of the sulfuric acid to give the protonated species. The protonated alcohol is now a good leaving group. Loss of  $\text{H}_2\text{O}$  occurs to give a carbocation, followed by loss of an adjacent proton. This is an elimination reaction. Note that  $\text{H}_3\text{O}^+$  is regenerated in the final step so that the  $\text{H}_3\text{O}^+$  is not used up in the reaction.

As you see in Figure 5.1, all steps in this conversion are reversible: cyclohexene, water and acid react to give cyclohexanol. The procedure works only because the pot temperature is about  $160\text{ }^\circ\text{C}$ . As soon as cyclohexene and water are formed, they evaporate and are removed from the acid solution. Sulfuric acid has a very high boiling point.

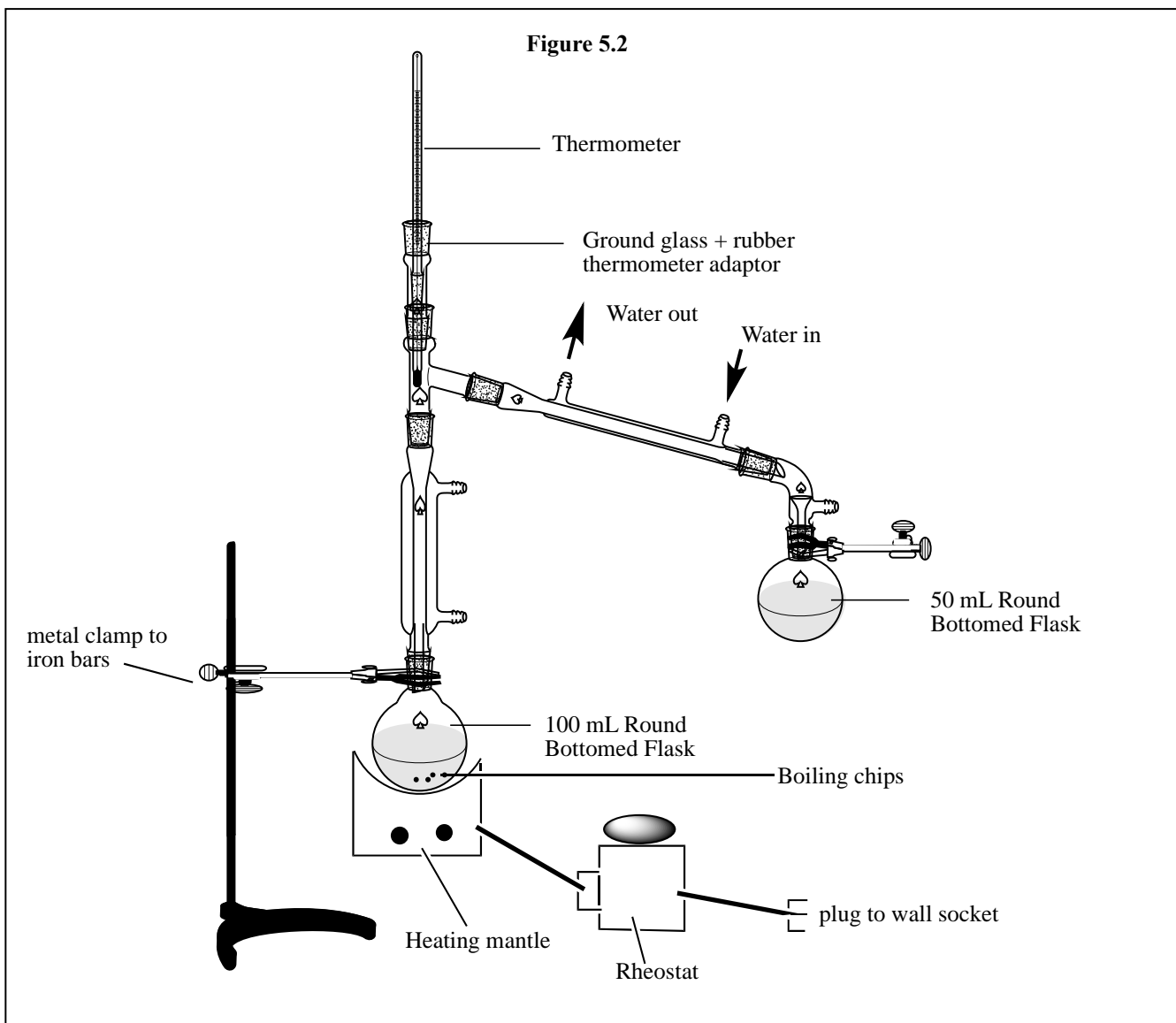
### Physical Constants

Compound	Mol. Wt (g/mol)	Density (g/mL)	b.p. ( $^\circ\text{C}$ )	m.p. ( $^\circ\text{C}$ )
Cyclohexanol	100.16	0.96	161.5	25.5
Cyclohexene	82.15	0.811	83	-104
Sulfuric acid	98.08	1.840	330	

### Experimental Procedure and Set-up

The set-up for the apparatus is shown in Figure 5.2. First, add 10 mL cyclohexanol to a clean, dry 100 mL round bottom flask. Add 2-3 boiling chips and then add about 0.5 mL concentrated sulfuric acid (about 10 drops). Swirl thoroughly to mix the contents. At this point it is normal to see a bit of yellow color. Clamp the 100 mL round bottom flask in place as shown in Figure 5.2. Add your distilling column, the three-way adapter, your thermometer and ground glass thermometer adapter and the condensing column, vacuum adapter and 50

mL round bottom as shown in the figure. Heat with a heating mantle at 90 volts. An ice bath to cool the receiving flask is recommended so as to keep the vapors of cyclohexene to a minimum in the laboratory.



You will distill over a mixture of cyclohexene and water. You should see two layers but since cyclohexene has some solubility in water and water has some solubility in cyclohexene what you often see is a cloudy emulsion of the two liquids.

Continue the distillation until only a small residue remains in the reaction flask. Do not keep heating until the reaction flask is totally dry because there is always a bit of tarry residue (cyclohexene polymer) remaining in the reaction flask and over heating will cause this material to dry out and adhere to the walls of your flask so that cleaning of the flask becomes very difficult.

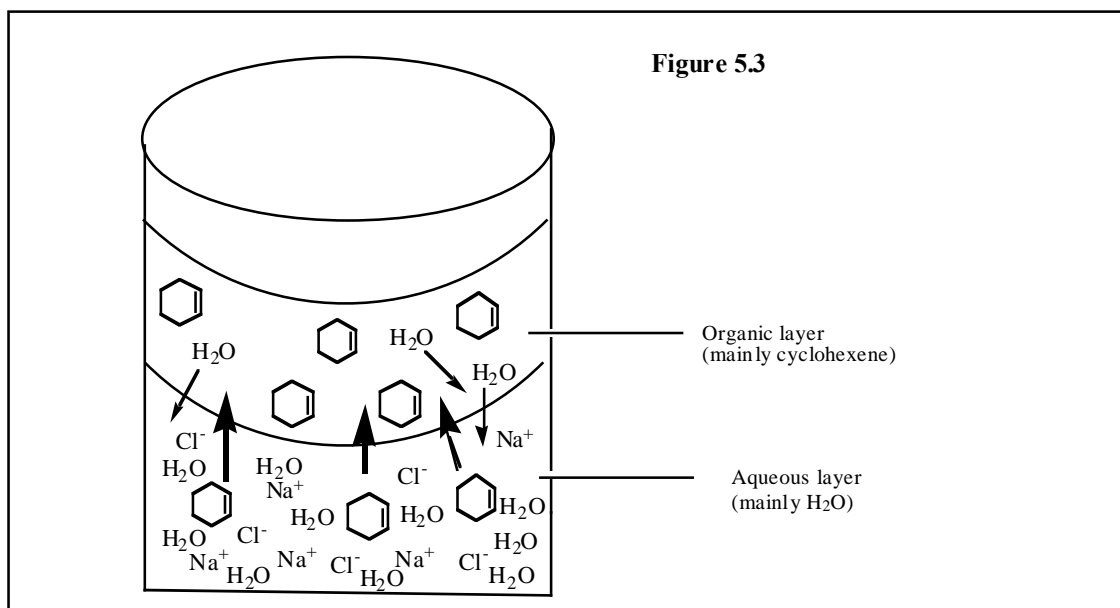
#### **Cleaning the reaction flask:**

Clean your reaction flask as soon as possible since the longer you wait, the harder it will be to clean it. Allow it to cool to or near room temperature. Add 5-10 mL acetone and with the wire brush (the blunt, rounded

end of your spatula also works) try to dislodge as much of the solid tarry residue as possible. This material is high molecular weight hydrocarbons created by the acid catalyzed polymerization of the cyclohexene product. It is fairly soluble in organic solvents but not soluble in water. The alcohol/KOH cleaning solution provided by the stockroom is also useful.

### Work-up

We will use the technique of **salting out** to get rid of the water that is partially dissolved in the cyclohexene layer and the cyclohexene that is dissolved in the water layer. Following the



rule of thumb that “like dissolves like”, we add sodium chloride to the mixture. It dissolves in the water and the presence of ions increases the ionic strength of the aqueous layer. Cyclohexene is relatively non-polar and it does not dissolve sodium chloride. By increasing the difference in polarity of the two layers, we “salt out” the organic material from the water layer. Likewise, any water that is in the cyclohexene layer is drawn to the water layer as the ionic strength of the water increases.

To the receiving flask (the 50 mL round bottom) add solid sodium chloride until no more sodium chloride will dissolve. How much sodium chloride is this? There is no fixed amount. Get a small amount of sodium chloride (1-2 g) on a watch glass. Add a spatula tip of the solid NaCl and with your spatula stir vigorously to get the sodium chloride to dissolve. It is very important to mix the two layers thoroughly with your spatula. When all of the sodium chloride has dissolved, add another spatula tip and dissolve this material using your spatula to stir/mix vigorously. Again, make sure the two layers mix thoroughly. Continue doing this until you see some solid sodium chloride remaining in the bottom of the flask. At this point the top organic layer (this is your product) should have become much clearer than it was and also the bottom layer (this is the water layer) should have separated fully.

Add 1-2 mL of 10% sodium bicarbonate solution so as to neutralize any sulfuric acid that may be contaminating the product. The water should be tested with red litmus paper to be sure that it turns slightly blue. Since the water layer is on the bottom, a small amount must be removed with a medicine dropper and placed on the litmus strip. Never place the indicator strips into a product. Always remove a drop and place it on the strip. Litmus only responds to water solutions.

Carefully decant the two layers (the cyclohexene and the water) into your separatory funnel. Remember to put a small beaker under your separatory funnel to catch any spills. Be careful not to transfer any solid sodium chloride into the separatory funnel as it can clog the small hole in the stopcock. If this happens do not panic. Adding 1-2 mL of water and slowly tilting the separatory funnel back and forth will usually solve this problem. Ask your instructor for guidance.

Drain off the bottom, aqueous layer. (Be sure to save it until you are done with the experiment and are sure that you have isolated the correct layer). Pour the top organic layer into a dry 50 mL Erlenmeyer flask. Cover the bottom with calcium chloride drying agent (see Appendix 3.2 for the proper use of drying agents). Cover the Erlenmeyer with a cork and allow it to stand for 10-15 minutes with occasional stirring while you set up the apparatus for a simple distillation.

Decant your cyclohexene product into a clean, dry 50 mL round bottom flask, add 2-3 boiling chips and set up your apparatus similar to Figure 5.4. Use a clean, dry 25 mL flask to collect your product. In this final distillation, instead of using a heating mantle, a bath of boiling water may be used as the source of heat. Use hot water from the tap and your metallic pot for this purpose and heat with a flame. This set up is sometimes described as a "bain Marie" (Mary's bath), apparently after a rather accomplished French alchemist who reasoned that this is the best way of heating things gently. Distillation from boiling water ensures that only cyclohexene will be distilled (b.p. 82 °C). Other possible contaminants (water, cyclohexanol, sulfuric acid) will not boil at the temperature of boiling water. Collect the fraction that boils from 79-85 °C. Pour this material in a pre-weighed vial, determine its weight, and turn this in to the teaching assistant. Record the weight in your notebook and calculate the percent yield. Turn in the Yield Report sheet.

